

- ($\lambda = 0.71073 \text{ \AA}$). Data were collected at room temperature ($\omega/2\theta$ -scan mode). For both compounds, unit-cell dimensions were determined from the angular setting of 25 reflections. Intensity data were corrected for Lorentz and polarization effects. Semiempirical absorption correction (ψ -scan)^[3a] was applied. For **1**-PF₆, this procedure by itself was not adequate enough. The difference Fourier map still showed peaks up to $3.6 \text{ e \AA}^{-3}$ close to the Ir atom. Therefore an additional absorption correction was applied using the DIFABS procedure,^[3b] resulting in final residual peaks up to $2.3 \text{ e \AA}^{-3}$. The structures were solved by the program system DIRDIF^[3c] using the program PATTY^[3d] to locate the heavy atoms, and were refined with standard methods (refinement against F^2 of all reflections with SHELXL-97^[3e] with anisotropic parameters for the non-hydrogen atoms. The hydrogen atoms were initially placed at calculated positions, refined isotropically in riding mode, and were subsequently refined freely. For **1**-PF₆, based on geometrical considerations alone, the unit cell could be transformed to an orthorhombic C-cell ($a = 9.1795(19)$, $b = 46.2562(78)$, $c = 11.5840(17) \text{ \AA}$), but this transformation is not supported by the symmetry of the data ($R_{\text{int}} = 0.549$) nor by the unit-cell contents. From the anisotropic thermal displacement parameters for the PF₆ moieties of **2**-(PF₆)₂, it is clear that some atoms show a large positional disorder. Although it is possible to use several partially occupied positions for these atoms, no physically reasonable models result from these parameters, at least not any that are better than the models presented here. Summary of the crystal data for **1**-PF₆: (C₂₃H₂₆N₄PF₆Ir, $M_r = 697.66$): monoclinic, space group $P2_1/c$, $a = 9.1802(19)$, $b = 11.5828(18)$, $c = 23.581(4) \text{ \AA}$, $\beta = 101.193(19)^\circ$, $V = 2459.7(7) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calc}} = 1.884 \text{ g cm}^{-3}$. Final R indices: $R_1 = 0.0529$ (for 3815 reflections considered observed [$I > 2\sigma(I)$]), $wR_2 = 0.1314$ (all data) for the 319 total variables. Summary of the crystal data for **2**-(PF₆)₂: (C₂₃H₂₆N₄P₂F₁₂Ir, $M_r = 842.63$): monoclinic, space group $P2_1/a$, $a = 13.072(2)$, $b = 12.454(2)$, $c = 18.860(3) \text{ \AA}$, $\beta = 109.734(11)^\circ$, $V = 2890.0(8) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calc}} = 1.937 \text{ g cm}^{-3}$. Final R indices: $R_1 = 0.0393$ (for 5292 reflections considered observed [$I > 2\sigma(I)$]), $wR_2 = 0.1011$ (all data) for the 382 total variables. a) A. C. T. North, D. C. Philips, F. S. Mathews, *Acta Crystallogr. Sect. A* **1968**, *24*, 351; b) N. Walker, D. Stuart, *Acta Crystallogr. Sect. A* **1983**, *39*, 158; c) P. T. Beurskens, G. Beurskens, W. P. Bosman, R. de Gelder, S. Garcia-Granda, R. O. Gould, R. Israel, J. M. M. Smits, DIRDIF-96, A computer program system for crystal structure determination by Patterson methods and direct methods applied to difference structure factors; Crystallography Laboratory, University of Nijmegen (The Netherlands), **1996**; d) P. T. Beurskens, G. Beurskens, M. Strumpel, C. E. Nordman in *Patterson and Pattersons* (Eds.: J. P. Glusker, B. K. Patterson, M. Rossi), Clarendon, Oxford, **1987**, p. 356; e) G. M. Sheldrick, SHELXS-97, Program for the refinement of crystal structures, University of Göttingen, Göttingen (Germany), **1997** CCDC-176107 for **1**-PF₆ and CCDC-176108 for **2**-(PF₆)₂ contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
- [4] Organic π radicals normally show much weaker superhyperfine coupling with H nuclei, e.g. C₂H₅⁺ radical: 70 MHz; allyl free radical: 11–42 MHz; naphthalene anion radical: 5–13 MHz. B. H. J. Bielski, J. M. Gebicki, *Atlas of Electron Spin Resonance Spectra*, Academic Press, New York, **1967**.
- [5] Geometries were optimized at the B3LYP level^[12] by using the Gaussian98 suite of programs.^[13] Basis sets used include the LANL2DZ basis and pseudo potential^[14] for the iridium center and STO3G^[15] on all other atoms. The orbitals presented here were visualized using the Molden program (see Supporting Information).^[16]
- [6] D. G. DeWit, *Coord. Chem. Rev.* **1996**, *147*, 209–246, and references therein.
- [7] K. K. Pandey, *Coord. Chem. Rev.* **1992**, *121*, 1–42, and references therein.
- [8] M. P. Garcia, M. V. Jimenez, L. A. Oro, F. J. Lahoz, P. J. Alonso, *Angew. Chem.* **1992**, *104*, 1512–1514; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1527–1529.
- [9] H. L. Zhai, A. Bunn, B. Wayland, *Chem. Commun.* **2001**, 1294–1295.
- [10] Other formylmethyl M^{III} species (M = Rh, Ir) have been reported: a) D. Milstein, J. C. Calabrese, *J. Am. Chem. Soc.* **1982**, *104*, 3773–

- 37741; b) B. de Bruin, J. A. W. Verhagen, C. H. J. Schouten, A. W. Gal, D. Feichtinger, D. A. Plattner, *Chem. Eur. J.* **2001**, *7*, 416–422; c) M. Krom, R. G. E. Coumans, J. M. M. Smits, A. W. Gal, *Angew. Chem.* **2002**, *114*, 595–599; *Angew. Chem. Int. Ed.* **2002**, *41*, 576–579.
- [11] During conversion of **2** into **3** at -10°C in acetone:MeOH (2:3) some decomposition of **3** occurs. At approximately 50% conversion, **3** was present in about 40% of the initial spin concentration. At full conversion, **3** was present in around 30% of the initial spin concentration. Attempts to record EPR spectra of **2** and **3** in MeCN yielded very broad spectra, probably because of the poor quality of the MeCN glass and/or crystallization. However, despite the broadness of the signals, aerated samples of **2** in MeCN show EPR peaks at the same positions as those for **2** and **3** in acetone:MeOH (2:3).
- [12] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789; c) B. Miehlich, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett.* **1989**, *157*, 200–206.
- [13] Gaussian98 (Revision A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**.
- [14] a) W. J. Hehre, R. F. Stewart, J. A. Pople, *J. Chem. Phys.* **1969**, *51*, 2657–2664; b) J. B. Collins, P. v. R. Schleyer, J. S. Binkley and J. A. Pople, *J. Chem. Phys.* **1976**, *64*, 5142–5151.
- [15] a) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 270–283; b) W. R. Wadt, P. J. Hay, *J. Chem. Phys.* **1985**, *82*, 284–298; c) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299–310.
- [16] G. Schaftenaar, J. H. Noordik, *J. Comput.-Aided Mol. Des.* **2000**, *14*, 123–134.

A Highly Regioselective Synthesis of Polysubstituted Naphthalene Derivatives through Gallium Trichloride Catalyzed Alkyne–Aldehyde Coupling**

Ganapathy S. Viswanathan, Mingwen Wang, and Chao-Jun Li*

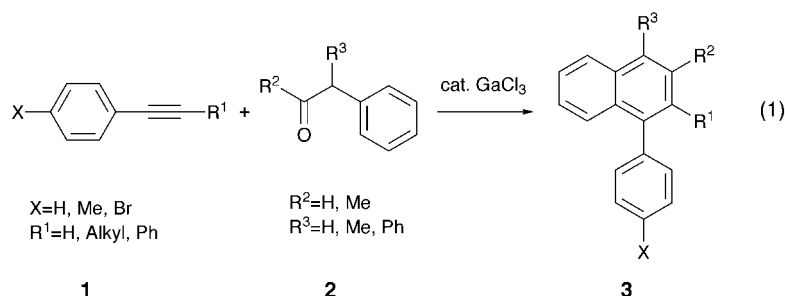
Polysubstituted aromatic compounds have played an important role in the chemical and pharmaceutical industries as well as in the fields of optical and electronic materials. Traditionally, the regioselective construction of polysubstituted aromatic compounds has been carried out by the stepwise introduction of substituents through electrophilic substitutions.^[1] More modern achievements in the regioselective

[*] Prof. Dr. C.-J. Li, G. S. Viswanathan, Dr. M. Wang
Department of Chemistry, Tulane University
New Orleans, LA 70118 (USA)
Fax: (+1) 504-865-5596
E-mail: cjli@tulane.edu

[**] This work has been partially supported by the US NSF CAREER Award program and the US NSF-EPA STAR program.

Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

construction of aromatic compounds include the direct *ortho*-metallation,^[2] transition-metal-catalyzed [2+2+2] alkyne cyclizations,^[3, 4] and Bergman-type^[5b-i] (thermal and catalyzed) cyclization of enediynes.^[5a-g, 4] Other important methods include the [4+2] cyclizations.^[4] Recently, there has been considerable interest in synthesizing naphthalene derivatives and other extended aromatic systems, which are extremely useful benzenoid compounds for biological studies and material applications. The most important methods include annulation via Fischer carbenes (the Dötz reaction)^[6] and palladium-catalyzed cyclization of alkynes with arylsilyl triflates via highly reactive benzyne (generated in situ).^[7] Another method is based on the cyclopropane-shift type reaction,^[8] which produces naphthalene derivatives only as by-products. Herein, we wish to report a hitherto unknown cyclization reaction between aromatic alkynes **1** and phenyl acetaldehydes **2** catalyzed by gallium trichloride^[9] to give naphthalene derivatives **3** with complete regioselectivity of all substituents [Eq. (1)].



Recently, we reported a unique coupling reaction between aromatic alkynes and aldehydes resulting in α , β -unsaturated ketones and cyclization products.^[10] In our efforts to obtain better selectivity in the formation of either of these products, we investigated the reaction between 1-phenyl-1-propyne (**1b**) and phenylacetaldehyde (**2a**) in methylene chloride in the presence of gallium trichloride (1 equiv). Surprisingly, neither expected product was obtained. Instead, a new product with a molecular weight of 218 (as shown by the GC/MS analysis of the crude reaction mixture) was obtained. Upon purification and characterization, the new product appeared to be 1-phenyl-2-methylnaphthalene (**3b**) (isolated in 41 % yield). Encouraged by this result, efforts were made to improve the yield of this novel coupling reaction (Table 1).

To begin the optimization, the effect of the amount of catalyst on the reaction was studied. When 1-phenyl-1-propyne (**1b**) was treated with phenylacetaldehyde (**2a**) in dichloromethane with gallium trichloride (1 equiv), the reaction went to completion (as was evident by the absence of the alkyne on TLC) after stirring overnight. However, the yield of the isolated product was only 41 % (Table 1, entry 1). A decrease in the amount of catalyst from 100 mol % to 5.8 mol % resulted in a better conversion (Table 1, entry 2). The same effect was also observed in the reaction of **2a** with 1-phenyl-1-pentyne (**1d**) (Table 1, entry 3). When less than 20 mol % of catalyst was used (Table 1, entries 2, 4, 6–10), although it took a relatively longer time for the alkynes to be consumed, the reactions were cleaner and yields were better

Table 1. Effect of the amount of catalyst, temperature, and solvent on the coupling reaction.

Entry	1 (X = H)	R ¹ =	2	R ² =	R ³ =	Catalyst [mol %]	Solvent	T [°C]	t [h]	3	Yield ^[a] [%]
1	b	Me	a	H	H	100.0	CH ₂ Cl ₂	RT	14	b	41
2	b	Me	a	H	H	5.8	CH ₂ Cl ₂	RT	39	b	55
3	d	Pr	a	H	H	90.7	CH ₂ Cl ₂	RT	36	d	26
4	d	Pr	a	H	H	5.5	CH ₂ Cl ₂	RT	42	d	50
5	b	Me	b	Me	Me	115.8	CH ₂ Cl ₂	RT	36	i	12
6	a	H	a	H	H	11.4	CH ₂ Cl ₂	RT	38	a	45
7	e	Bu	a	H	H	5.5	CH ₂ Cl ₂	RT	20	e	11
8 ^[b]	e	Bu	a	H	H	5.5	CH ₂ Cl ₂	reflux	20	e	52
9 ^[b,c]	e	Bu	a	H	H	5.5	toluene	50	13	e	41
10 ^[b]	e	Bu	a	H	H	5.5	CH ₂ Cl ₂	reflux	13	e	39

[a] Yields of isolated compounds. [b] The reactions were monitored by TLC and stopped after the alkyne had been consumed. [c] The reaction mixture was sonicated at 50 °C.

in all cases. At room temperature, the reaction of aliphatic alkynes with **2a** and a catalytic amount of gallium trichloride gave a complicated mixture, which is still under investigation.

To see the effect of different solvents and temperature on the yield, 1-phenyl-1-hexyne (**1e**) was chosen as a standard as it is relatively non-volatile and less reactive than **1b** and **1d**. When **1e** was treated with **2a** in the presence of a catalytic amount of gallium trichloride (5.5 mol %), 1-phenyl-2-butylnaphthalene (**3e**) was obtained in 11 % yield together with unreacted **1e** after 20 h of stirring in dichloromethane at room temperature (Table 1, entry 7). However, when **1e** was heated at reflux with **2a** in dichloromethane with gallium trichloride (5.5 mol %), after 20 h of stirring, the yield of **3e** increased to 52 % (Table 1, entry 8). Chloroform and toluene were also examined as solvents. Both gave lower yields of the desired product (Table 1, entries 9 and 10).

Subsequently, several aromatic alkynes were treated with substituted and unsubstituted phenyl acetaldehydes (Table 2). The yields of the isolated products ranged from 40–70 % for

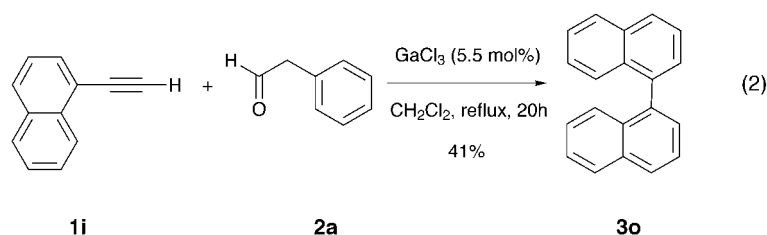
Table 2. Coupling of alkynes and carbonyl compounds to generate naphthalene derivatives.

Entry	1	X =	R ¹ =	2	R ² =	R ³ =	Catalyst [mol %]	t [h]	3	Yield ^[a] [%]
1	a	H	H	a	H	H	7.7	15	a	50
2	b	H	Me	a	H	H	7.8	16	b	61
3	c	H	Et	a	H	H	5.5	15	c	64
4	d	H	Pr	a	H	H	6.0	21	d	62
5	e	H	Bu	a	H	H	5.5	20	e	52
6	f	CH ₃	H	a	H	H	5.5	20	f	46
7	g	Br	H	a	H	H	5.5	20	g	49
8	a	H	H	b	H	Me	4.9	16	h	51
9	b	H	Me	b	H	Me	13.0	24	i	70
10	h	H	Ph	a	H	H	7.7	24	j	25 ^[b]
11	a	H	H	c	H	Ph	14.0	23	k	55 ^[c]
12	d	H	Pr	b	H	Me	8.6	14	l	63
13	c	H	Et	c	H	Ph	12.4	19	m	68
14	a	H	H	d	Me	Ph	15.3	54	n	10

[a] Yields of isolated compounds. [b] The crude reaction mixture contained a large amount of unreacted diphenylacetylene, even after heating at reflux for 24 h. [c] Yield at RT.

most substrates. NMR spectroscopic and GC/MS analysis of the other fractions obtained after column chromatography indicated a complicated mixture whose identity could not be determined. We believe that the rest of the starting materials could have been lost as a result of a competing polymerization reaction.

This gallium trichloride catalyzed coupling reaction produced a single regioisomer in all cases. This high regioselectivity was further confirmed by the reaction of 1-ethynyl-naphthalene (**1i**) and **2a** which gave 1,1'-binaphthalene (**3o**) (a symmetric compound) as the only product [Eq. (2)].



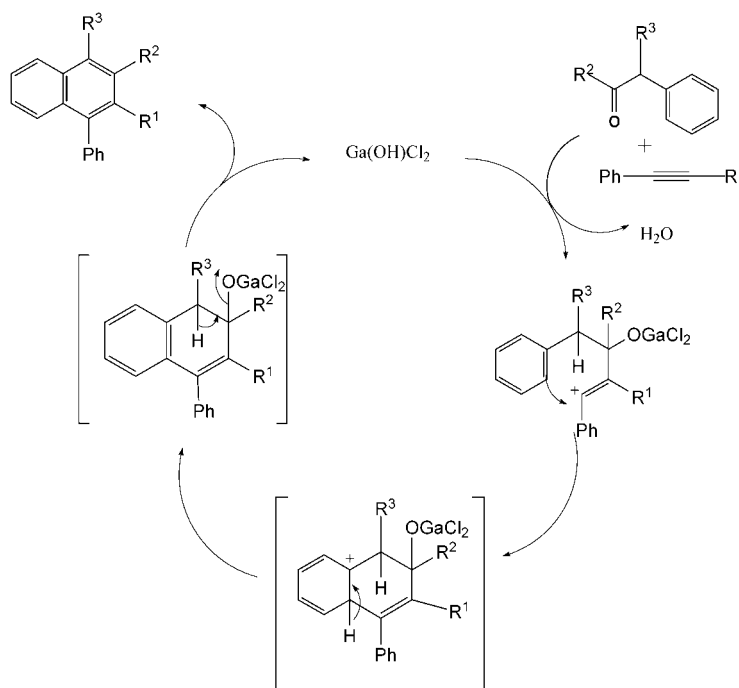
Apparently, varying the amount of catalyst from 4–15 mol% did not have any major impact on the yields of the desired products. Substituents on the aromatic ring of the phenyl alkynes also had no significant effect on the yields of the isolated naphthalene derivatives (Table 2). However, the yield was 10% lower for 1-ethynyl-naphthalene (**1i**) [eq. (2)] than for phenylacetylene (Table 2, entry 1). When the R^1 group of the alkyne was changed from H to methyl, ethyl, or *n*-propyl, the yield increased by about 10% (Table 2, entries 2–4), whereas when it was changed to phenyl, the yield as well as the rate of the reaction decreased (Table 2, entry 10). When the R^3 group of the aldehyde was changed from H to methyl or phenyl, the yield increased slightly (Table 2, entries 8, 9, 11–13). Phenylacetophenone (**2d**) was also effective under the reaction conditions; however, the yield was low (Table 2, entry 14) probably as a result of the increased steric effect of the ketone relative to the aldehyde. More interestingly, the reaction of 1-phenyl-1-propyne (**1b**) with **2d** generated the symmetrical tetra-substituted naphthalene derivative **3p**, albeit in very low yield (<5%), which is still being optimized [Eq. (3)].

When 1-phenyl-1-butyne (**1c**) was heated at reflux with **2a** and H_2O (2 equiv) in dichloromethane in the presence of catalyst CaCl_3 (5 mol%), the desired product was obtained in 65% yield. When the same reaction was

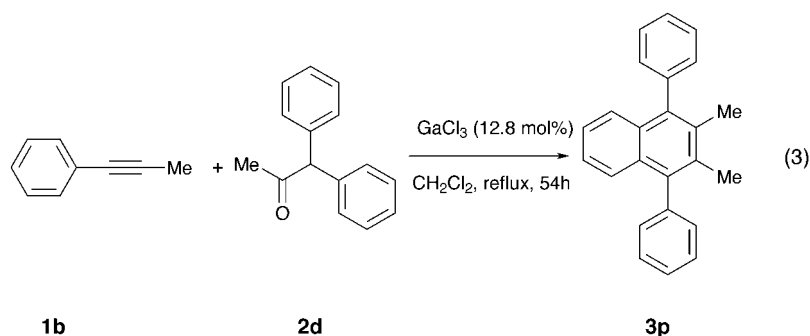
performed under relatively dry conditions under a nitrogen atmosphere, the yield dropped to 55%. As gallium trichloride is hydrolyzed very fast in air and the presence of water did not decrease the yield, we believe that the active catalyst could be gallium hydroxide dichloride. This is supported by our earlier work on gallium trichloride mediated coupling of alkynes and aldehydes to generate enones.^[10]

Based on the results, a tentative mechanism is proposed in Scheme 1. Gallium trichloride hydrolyzes in air to generate the active catalyst gallium hydroxide dichloride, which catalyzes the regioselective electrophilic addition of the aldehyde–Lewis acid complex to C2 of the 1-phenylalkyne.^[11] Intramolecular electrophilic attack of the formed alkenyl cation to the aromatic system followed by elimination of a proton generates the cyclization product, which aromatizes to form the corresponding naphthalene derivative and regenerates the active catalyst.

In summary, we have developed a new synthetic strategy to generate polysubstituted naphthalene derivatives with complete regioselectivity through



Scheme 1. Proposed mechanism for the formation of naphthalene derivatives.



the simple coupling of alkynes and phenyl acetaldehydes (and ketones) catalyzed by gallium trichloride under mild conditions.^[12] The scope, mechanism, and synthetic applications of this new reaction are under investigation.

Experimental Section

General procedure: Gallium trichloride (7.5 mg, 0.042 mmol, 6 mol%) was added to a solution of 1-phenyl-1-pentyne (**1d**, 101.5 mg, 0.70 mmol) and phenylacetaldehyde (**2a**, 110.9 mg, 0.92 mmol) in dichloromethane (3.5 mL). The solution turned dark red instantaneously. The reaction mixture was heated at reflux for 21 h. The

reaction mixture was concentrated in vacuo. Subsequently, the crude mixture was purified by column chromatography with hexane as eluent to give 1-phenyl-2-propylnaphthalene (**3d**, 106 mg, 0.43 mmol, 62 %).

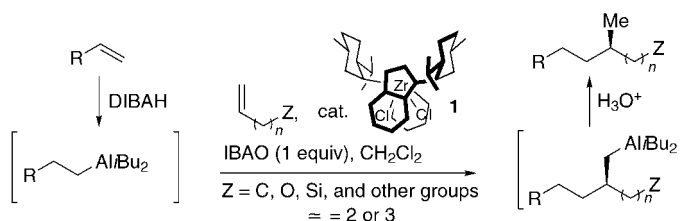
Received: January 28, 2002 [Z18598]

Revised: March 20, 2002

A New Protocol for the Enantioselective Synthesis of Methyl-Substituted Alkanols and Their Derivatives through a Hydroalumination/Zirconium-Catalyzed Alkylaluminum Tandem Process**

Shouquan Huo, Ji-cheng Shi, and Ei-ichi Negishi*

We report herein a new protocol for the Zr-catalyzed enantioselective carboalumination of alkenes^[1], which consists of a hydroalumination/alkylaluminum tandem process (Scheme 1). The most noteworthy significance of the protocol in synthetic applications is that it permits the asymmetric synthesis of methyl-substituted alkanols and other derivatives typically in 90–93 % *ee*, which represents an increase in *ee* values by roughly 15 % from the previously attainable 70–80 %.^[1–3]



Scheme 1. Hydroalumination/Zr-catalyzed enantioselective carboalumination/hydrolysis process for the synthesis of methyl-substituted alkanols. IBAO = isobutylaluminumoxane.

The development of the protocol has critically depended on the following recent findings. First, the primary alkyl groups of the RCH_2CH_2 type ($R = H$ or alkyl group) derived from $RCH=CH_2$ by in situ hydroalumination^[4] with iBu_2AlH (DIBAH) can participate selectively in the Zr-catalyzed enantioselective carboalumination; these alkyl groups compete directly with two equivalents of the iBu group and the isoalkyl group generated in the desired alkylaluminum. As the results summarized in Scheme 2 indicate, the reaction of n -decyldiisobutylalane (2 equiv^[5]) with $H_2C=CH(CH_2)_2OTBDPS$ in the presence of (–)-bis-(neomenthylindenyl)zirconium dichloride^[6] (**1**; 5 mol %, purified single isomer) in CH_2Cl_2 followed by protonolysis led to the formation of the desired product **2** in 80–84 % yields with 90–91 % *ee*.^[7] Only traces, if any, of the isobutylaluminated product **3** were formed. Similarly, there was no indication of the formation of dimeric and oligomeric products. The main byproduct was $nBuOTBDPS$, which must have been formed

- [1] J. March, *Advanced Organic Chemistry*, 4th ed., Wiley, New York, 1992, chap. 11, p. 501.
- [2] V. Snieckus, *Chem. Rev.* **1990**, 90, 879.
- [3] a) D. B. Grothahn in *Comprehensive Organometallic Chemistry II*, Vol. 12 (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson, L. S. Hegehus), Pergamon, Oxford, 1995, p. 741; b) M. Lautens, W. Klute, W. Tam, *Chem. Rev.* **1996**, 96, 49; c) W. Reppe, W. J. Schueckendiek, *Justus Liebigs Ann. Chem.* **1948**, 560, 104.
- [4] S. Saito, Y. Yamamoto, *Chem. Rev.* **2000**, 100, 2901, and references therein.
- [5] a) V. Gevorgyan, A. Takeda, M. Homma, N. Sadayori, U. Radhakrishnan, Y. Yamamoto, *J. Am. Chem. Soc.* **1999**, 121, 6391; b) N. Uchiyama, Y. Yamamoto, *J. Org. Chem.* **1998**, 63, 7022; c) V. Gevorgyan, A. Takeda, Y. Yamamoto, *J. Am. Chem. Soc.* **1997**, 119, 11313; d) V. Gevorgyan, N. Sadayori, Y. Yamamoto, *Tetrahedron Lett.* **1997**, 38, 8603; e) S. Saito, M. M. Salter, V. Gevorgyan, N. Tsuboya, K. Tando, Y. Yamamoto, *J. Am. Chem. Soc.* **1996**, 118, 3970; f) R. C. Burrell, K. J. Daoust, A. Z. Bradley, K. J. DiRico, R. P. Johnson, *J. Am. Chem. Soc.* **1996**, 118, 4218; g) R. L. Danheiser, A. E. Gould, R. F. Pradilla, A. L. Helgason, *J. Org. Chem.* **1994**, 59, 5514; h) R. G. Bergman, *Acc. Chem. Res.* **1973**, 6, 25; i) R. G. Bergman, R. R. Jones, *J. Am. Chem. Soc.* **1972**, 94, 660.
- [6] a) N. E. Shore, *Chem. Rev.* **1988**, 88, 1081; b) K. H. Dötz, *Angew. Chem.* **1984**, 96, 573; *Angew. Chem. Int. Ed. Engl.* **1984**, 23, 587.
- [7] a) E. Yoshikawa, K. V. Radhakrishnan, Y. Yamamoto, *J. Am. Chem. Soc.* **2000**, 122, 7280; b) D. Pena, D. Perez, E. Guitian, L. Castedo, *J. Am. Chem. Soc.* **1999**, 121, 5827; c) K. V. Radhakrishnan, E. Yoshikawa, Y. Yamamoto, *Tetrahedron Lett.* **1999**, 40, 7533; d) R. C. Larock, Q. Tian, *J. Org. Chem.* **1998**, 63, 2002; e) K. S. Feldman, R. E. Ruckle, Jr., S. M. Ensel, P. H. Weinreb, *Tetrahedron Lett.* **1992**, 33, 7101.
- [8] K. Wakasugi, Y. Nishii, Y. Tanabe, *Tetrahedron Lett.* **2000**, 41, 5937.
- [9] a) F. Yonehara, Y. Kido, S. Morita, M. Yamaguchi, *J. Am. Chem. Soc.* **2001**, 123, 11310; b) Y. Kido, F. Yonehara, M. Yamaguchi, *Tetrahedron* **2001**, 57, 827; c) J. Takaya, H. Kagoshima, T. Akiyama, *Org. Lett.* **2000**, 2, 1577, and references therein; d) N. Asao, T. Asano, T. Ohishi, Y. Yamamoto, *J. Am. Chem. Soc.* **2000**, 122, 4817; e) Y. Kido, S. Yoshimura, M. Yamaguchi, T. Uchimaru, *Bull. Chem. Soc. Jpn.* **1999**, 72, 1445; f) J. Su, S. D. Goodwin, X. W. Li, G. H. Robinson, *J. Am. Chem. Soc.* **1998**, 120, 12994; g) Y. Kido, M. Yamaguchi, *J. Org. Chem.* **1998**, 63, 8086.
- [10] G. S. Viswanathan, C. J. Li, *Tetrahedron Lett.* **2002**, 43, 1613.
- [11] a) D. J. Rodini, B. B. Snider, *Tetrahedron Lett.* **1980**, 21, 3857; b) U. Biermann, A. Lutzen, M. S. F. L. K. Jie, J. O. Metzger, *Eur. J. Org. Chem.* **2000**, 3069.
- [12] All products were characterized by ¹H and ¹³C NMR and IR spectroscopy, and by MS/elemental analysis.

[*] Prof. E.-i. Negishi, Dr. S. Huo, Dr. J.-c. Shi
Herbert C. Brown Laboratories of Chemistry, Purdue University
West Lafayette, IN 47907-1393 (USA)
Fax: (+1) 765-494-0239
E-mail: negishi@purdue.edu

[**] We thank the National Science Foundation (CHE-0080795), the National Institutes of Health (GM36792), and Purdue University for support of this research. We also thank Albemarle and Boulder Chemical for assistance in the procurement of Al and Zr compounds, respectively.

Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.